

AD-A014 067

RESEARCH ON ELECTROCHEMICAL ENERGY
CONVERSION SYSTEMS

Alayne A. Adams, et al

American University

Prepared for:

Army Mobility Equipment Research and
Development Center

March 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Research on Electrochemical Energy Conversion Systems		5. TYPE OF REPORT & PERIOD COVERED Sixth interim progress report April 1974 -Oct. 1974
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Adams, Alayne A. and Foley, Robert T.		8. CONTRACT OR GRANT NUMBER(s) DAAK02-72-C-0084
9. PERFORMING ORGANIZATION NAME AND ADDRESS The American University Washington, D.C. 20016		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1T161102A34A 03 100 FF
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia		12. REPORT DATE March 1975
		13. NUMBER OF PAGES 22 and iii 29
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release and sale; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electrochemistry, Fuel Cells, Electrolytes, Trifluoromethane sulfonic acid monohydrate, Phosphoric Acid		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The research on electrochemical energy conversion systems has involved work on two tasks. a search for electrolytes alternative to phosphoric acid for direct and indirect hydrocarbon-air fuel cells, and a study of the corrosion characteristics of electrolytes for intermediate-temperature hydrocarbon-air fuel cells. The effort during this reporting period has been concentrated on the		

DD FORM 1473

EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

first task and the experimental work has included the further investigation of the electrochemical behavior of trifluoromethane sulfonic acid monohydrate as a fuel cell electrolyte. Two questions were considered. The first dealt with the utilization of methanol as a fuel, both from its electrooxidation at a platinum electrode and from its tendency to interfere with the air electrode. Methanol dissolved in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ was electrooxidized over a temperature range of 23°C to 135°C with the highest rate being in the neighborhood of 80°C . At temperatures above 100°C vaporization losses are excessive even though an nmr study showed that the methanol is completely esterified at temperatures as low as room temperature. Methanol interferes with the air electrode, lowering both the open circuit potential and the limiting current density.

The electrochemical activities of hydrogen, propane, and air were investigated at a platinum electrode in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ at 23°C . In all three cases, the limiting currents were considerably lower than those observed at 135°C but the current levels might be such as to warrant engineering interest in a low temperature cell.

ia

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

<u>Table of Contents</u>	<u>Page</u>
Summary	i
Foreword	ii
List of Figures	iii
1.0 Introduction	1
2.0 Task I. A Search for Alternative Electrolytes to Phosphoric Acid for Direct and Indirect Hydrocarbon- Air Fuel Cells	
2.1 Introductory	1
2.2 Experimental	3
2.2.1 Preparation of Electrolytes	3
Trifluoromethanesulfonic acid monohydrate	3
Phosphoric acid (85%)	4
2.2.2 Apparatus and Techniques	4
Electrochemical studies	4
Nuclear magnetic resonance studies	6
2.3 Results	
The effect of flow rate on the air electrode	6
Electrochemical reduction of air at ambient temperature - current-potential diagrams	6
Electrochemical oxidation of hydrogen at ambient temperature - current-potential diagrams	9
Electrochemical oxidation of propane at ambient temperature - current-potential diagram	9
Electrooxidation of Methanol	13
Nuclear Magnetic Resonance Measurements	16
2.4 Conclusions	20
3.0 Future Work	21
4.0 References	22

SUMMARY

The research on electrochemical energy conversion systems has involved work on two tasks: a search for electrolytes alternative to phosphoric acid for direct and indirect hydrocarbon-air fuel cells, and a study of the corrosion characteristics of electrolytes for intermediate-temperature hydrocarbon-air fuel cells.

The effort during this reporting period has been concentrated on the first task and the experimental work has included the further investigation of the electrochemical behavior of trifluoromethanesulfonic acid monohydrate as a fuel cell electrolyte. Two questions were considered. The first dealt with the utilization of methanol as a fuel, both from its electrooxidation at a platinum electrode and from its tendency to interfere with the air electrode. Methanol dissolved in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ was electrooxidized over a temperature range of 23°C to 135°C with the highest rate being in the neighborhood of 80°C . At temperatures above 100°C vaporization losses are excessive even though an mnr study showed that the methanol is completely esterified at temperatures as low as room temperature. Methanol interferes with the air electrode, lowering both the open circuit potential and the limiting current density.

The electrochemical activities of hydrogen, propane, and air were investigated at a platinum electrode in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ at 23°C . In all three cases the limiting currents were considerably lower than those observed at 135°C but the current levels might be such as to warrant engineering interest in a low temperature cell.

FOREWORD

This research on electrochemical energy conversion systems has been sponsored by the U.S. Army Mobility Equipment Research and Development Center at Fort Belvoir, Virginia under Contract No. DAAK02-72-C-0084 with The American University. The work was authorized under DA Project/Task area/Work Unit No. 1T161102A34A 03 100 EF.

List of Figures

	<u>Page</u>
Figure 1. Relationship between open-circuit potential and flow rate of air. (Electrolyte $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, temperature 135°C .)	7
Figure 2. Relationship between limiting current density and flow rate of air (Electrolyte $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, temperature 135°C , potential 0.8 v.)	8
Figure 3. Current-potential diagrams for the air electrode at 23°C . X, 85% H_3PO_4 ; \blacklozenge , $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$.	10
Figure 4. Current-potential diagrams for the hydrogen electrode at 23°C . X, 85% H_3PO_4 ; \bullet , $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	11
Figure 5. Current-potential diagram for the electrooxidation of propane in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ at 23°C .	12
Figure 6. Current-potential diagrams for the electrooxidation of methanol. \blacksquare , 23°C ; \bullet , 80°C ; \square , 115°C ; \bigcirc , 135°C ; X data from reference 5.	14
Figure 7. Electroreduction of oxygen in the presence of methanol: \bullet Air - $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ at 23°C ; \bigcirc , Air - $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ - 1M MeOH at 23°C ; \square Air - $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ - 1M MeOH at 95°C ; X, Air - $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ - 1M MeOH at 115°C ; \times , Air - $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ at 115°C .	17
Figure 8. Pertinent parts of nmr spectra of solution of methanol in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$.	18
Figure 9. Comparison of peaks in nmr spectra. Right, methyl peak due to CH_3OH ; left, methyl peak due to one molar methanol- $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ mixture. Shift is 0.644 ppm.	19

1.0 Introduction

This is the sixth semi-annual report on Contract No. DAAK02-72-C-0084 sponsored by the U.S. Army Mobility Equipment Research and Development Center at Fort Belvoir, Virginia. The project entitled "Research on Electrochemical Energy Conversion Systems", consists of two technical tasks, both of which are directed toward the improvement of the hydrocarbon-air fuel cell for ground power systems and vehicular propulsion.

Task I. A search for alternative electrolytes to phosphoric acid for direct and indirect hydrocarbon-air fuel cells

Task II. A study of the corrosion characteristics of electrolytes for intermediate-temperature hydrocarbon-air fuel cells.

During this reporting period technical effort was expended on Task I involving further investigation of the properties of trifluoromethanesulfonic acid monohydrate as a fuel cell electrolyte.

2.0 Task I. A Search for Alternative Electrolytes to Phosphoric Acid for Direct and Indirect Hydrocarbon-Air Fuel Cells

2.1 Introductory

Previous work on this project has indicated that a new electrolyte, trifluoromethanesulfonic acid monohydrate, has certain physical and electrochemical properties which would make it an improved electrolyte over phosphoric acid. The deficiencies of phosphoric acid as a fuel cell electrolyte have been tabulated (1). The search for an "ideal" electrolyte has been guided by a list of properties or characteristics desired of a fuel cell electrolyte.

- a. the electrolyte should be a good medium for the efficient oxidation of the hydrocarbon
- b. the electrolyte should be a good medium for ionic charge transport
- c. the electrolyte should be a good solvent for active materials, e.g., propane, oxygen, water
- d. the electrolyte should be a good medium for material transport, e.g., removal of CO_2 , as rejection from an acid solution
- e. the electrolyte should be chemically and electrochemically stable over the temperature and voltage operating range of the fuel cell
- f. the electrolyte should possess suitable physical properties, e.g., viscosity and vapor pressure
- g. the electrolyte should not interfere with catalytic reactions, i.e., through anion adsorption or poisoning
- h. the electrolyte should be a good medium for the air electrode, and finally
- i. the electrolyte should not be strongly reactive to construction materials or the fuel cell matrix material.

At this point it is not possible to express these characteristics in a quantitative manner. For example, it is not possible to assign a critical figure for the hydrocarbon solubility because other mass transport parameters are not known. However, with the above list of properties in mind certain classes of chemical compounds are suggested as possible alternatives to phosphoric acid (1).

a. sulfonic acids, e.g., $\text{CF}_3\text{SO}_3\text{H}$ (the hydrate concept became apparent as the work progressed).

b. alpha-halo disubstituted carboxylic acids, e.g., CHCl_2COOH

c. perfluorocarboxylic acids, e.g., $\text{C}_2\text{F}_5\text{COOH}$

d. dialkyl phosphate esters, e.g., $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{OH}$

e. polyphosphates, e.g., Graham's salt

During the last reporting period (2) the anodic reaction of propane in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ was studied using potential ramp and cyclic voltammetric techniques. Current-potential diagrams for the reduction of air in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, at various temperatures from 90° to 135°C , on smooth platinum, were compared with similar data obtained in 85% H_3PO_4 .

During the present reporting period the effect of the gas flow rate on the performance of the air electrode was investigated at 135°C . Current-potential diagrams for air, propane and hydrogen were constructed at ambient temperature in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ and these diagrams were compared with similar data obtained with 85% H_3PO_4 . The investigation of the reaction of methanol in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ was begun with the development of current-potential diagrams and the use of the nuclear magnetic resonance (nmr) technique.

2.2 Experimental

2.2.1 Preparation of Electrolytes

Trifluoromethanesulfonic acid monohydrate

Trifluoromethanesulfonic acid monohydrate was prepared from the trifluoromethanesulfonic acid (3 M Corporation, Fluorochemical Acid FC-24, Lot 17) and water by the method of Gramstad and Haszeldine (3).

This method which involves successive distillations produced the acid monohydrate as a white, needle-like crystalline product with a sharp melting point at 34°C in agreement with the above referenced work.

Phosphoric acid (85%)

Phosphoric acid (Fisher, 85% ACS Grade) was further purified by the technique previously described (4). In this technique the commercial acid is treated with 30% H_2O_2 , concentrated, rediluted to 85% acid, and finally pre-electrolyzed. This 85% H_3PO_4 was used as a comparison electrolyte to evaluate results obtained with the $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ electrolyte.

2.2.2 Apparatus and Techniques

Electrochemical studies

The electrochemical cell and reference system have been described in an earlier progress report (1). The cell was a standard three-compartment cell of approximately 30 ml capacity to conserve the volume of the expensive electrolyte required per experiment. The technique used to electrochemically clean the electrolyte before the electrooxidation or electroreduction, as well as the method used to determine the surface area of the electrode were similar to those described in the referenced progress report.

Helium, propane, and air were used in different experiments. Helium (AIRCO) was passed over hot copper turnings to remove traces of oxygen before being passed into the cell. Propane (Matheson "Instrument" Grade) and Air (Air Products, "Breathing Quality") were used without pretreatment. All gas lines, which were Teflon tubing, were heated so that the gases as they entered the cell were close to the operating

temperature of the cell. The cell itself was maintained at temperature in an air oven.

The methyl alcohol used was Allied Chemical, General Chemical Division, reagent grade. The methyl alcohol solutions were prepared to 1 molar methyl alcohol in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$.

When phosphoric acid was used as the electrolyte it was necessary to humidify the gases before they were passed into the electrochemical cell. This was accomplished with a two compartment pyrex humidifier maintained at a temperature adequate to replace the water lost by the phosphoric acid (initially 85%) in the cell.

The electrochemical reactions of propane, hydrogen, and air were studied in both electrolytes. Current-potential measurements were made for the reactions in 85% H_3PO_4 and $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ at 23°C . The electronic apparatus has been described previously (4). In making these current-potential measurements the practice was to set the potential and then allow the system to equilibrate for five minutes before reading the value of the current. Current-potential measurements were found to reach a steady state more rapidly if the cell was run with air overnight under a potential of approximately 0.90 v vs the dynamic hydrogen electrode. (All potentials given in this report are with reference to the dynamic hydrogen electrode). In constructing the potential-current curve it was customary to use a constant potential difference-patterned sequence for the potentials as described in the previous report (2). After two or three runs the patterned sequence resulted in reproducible potential diagrams whereas a technique using consecutive potential increments might take as many as four to five runs to develop reproducible potential-current diagrams.

Nuclear magnetic resonance studies

NMR experiments were run on methanol- $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ mixtures at room temperature. A Varian A-60 NMR Spectrometer was employed with a tetramethyl silane external reference.

2.3 Results

The effect of flow rate on the air electrode

The investigation of the air electrode in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ was extended to ascertain the effect of the flow rate of air on the open circuit potential and the limiting current of the electrode. The relationship between the open circuit potential and the flow rate at 135°C is shown in figure 1. Above a flow rate of 20 ml/minute the open circuit potential is essentially independent of flow rate attaining a value of 1.13 v. Below 20 ml/minute the potential drops off and is erratic.

The relationship between limiting current density and the flow rate of air at 135°C is shown in figure 2. The limiting current density was not greatly affected by the flow rate. The value for the limiting current density varied by only $6 \mu\text{a}/\text{cm}^2$ from a flow rate of 3 ml/min to a flow rate of 40 ml/min. From 20 ml/min to 70 ml/min the limiting current density varied only by $3 \mu\text{a}/\text{cm}^2$ which is within the range of experimental error.

Electrochemical reduction of air at ambient temperature - current-potential diagrams

A fuel cell operating without auxillary heating would offer obvious engineering advantages. With this in mind data were taken on the electrochemical reactions of air, propane and hydrogen at room temperature (23°C). These results were compared with those obtained in 85% H_3PO_4 at room temperature.

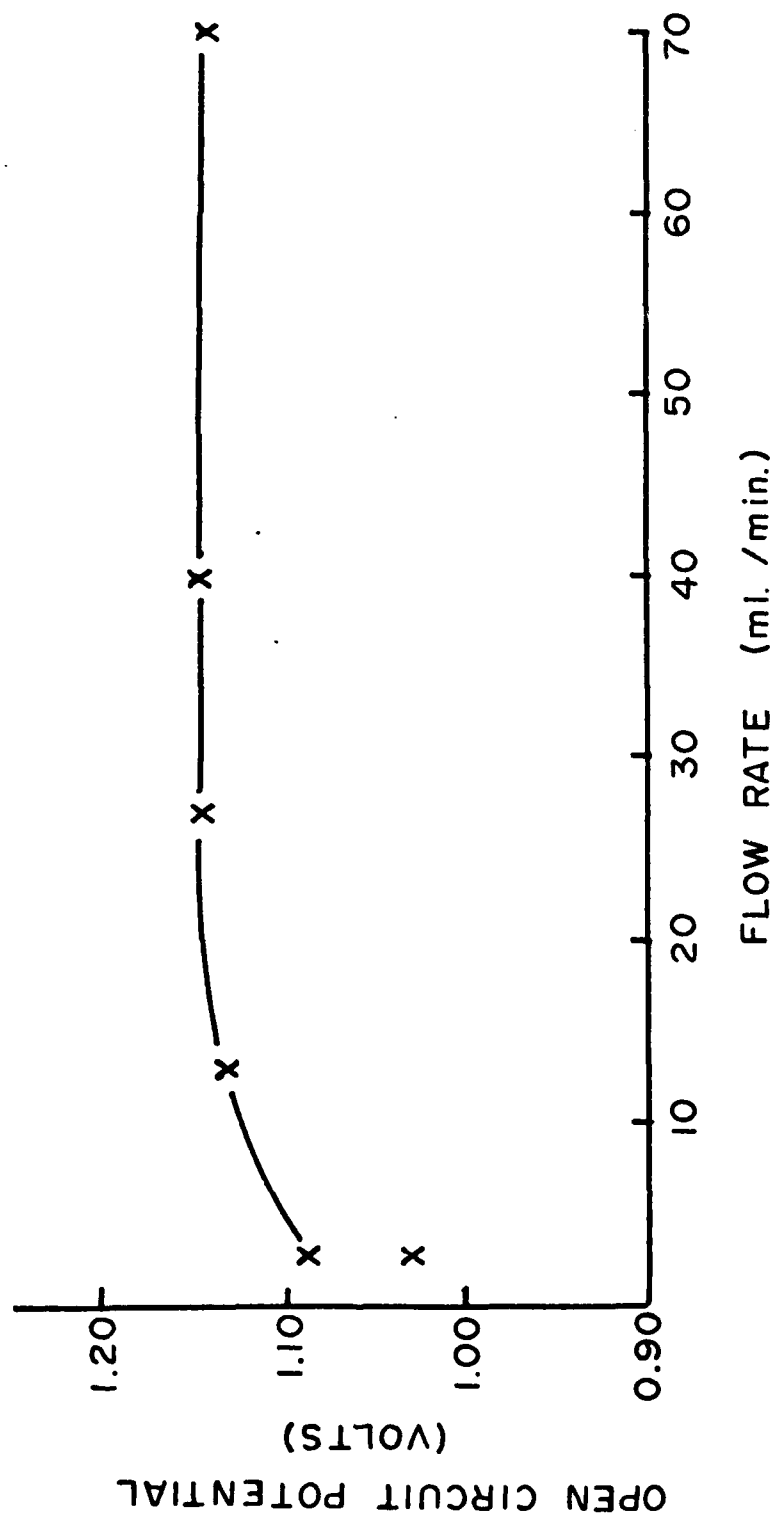


Figure 1. Relationship between open-circuit potential and flow rate of air. (Electrolyte $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, temperature $135^\circ\text{C}.$)

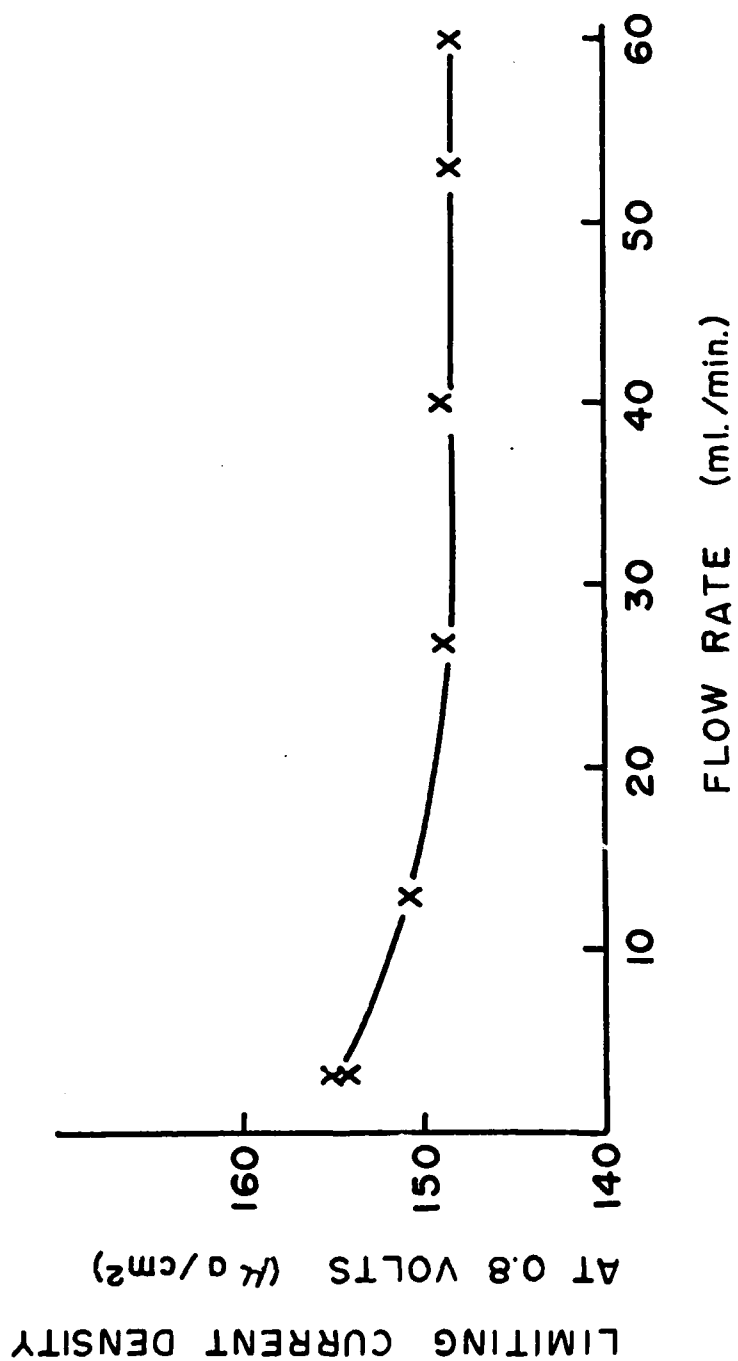


Figure 2. Relationship between limiting current density and flow rate of air (Electrolyte $CF_3SO_3H \cdot H_2O$, temperature $135^\circ C$, potential 0.8 v.)

Figure 3 compared the current density-potential diagram for air in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ with that for air in 85% H_3PO_4 . At room temperature the open circuit potential for air in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ is approximately 1.13 volts as compared to an open circuit potential of approximately 0.98 volts for air in H_3PO_4 . This is comparable to results obtained at higher temperatures (2). The limiting current density is slightly higher for air in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ than for air in 85% H_3PO_4 - $4.4 \mu\text{a}/\text{cm}^2$ as compared to $2.8 \mu\text{a}/\text{cm}^2$. The significant feature seen in the comparison of the two electrolytes at 23°C is the higher open circuit potential. The limiting current density was much higher at higher temperatures as would be expected.

Electrochemical oxidation of hydrogen at ambient temperature - current-potential diagrams

Figure 4 shows current density-potential plots for the oxidation of hydrogen in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ and in 85% H_3PO_4 at room temperature. The open circuit potential for hydrogen in both acids is 0.0 volts. The limiting current density value is produced in H_3PO_4 at a lower potential than in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$. The limiting current value is reached after approximately 60 mv in 85% H_3PO_4 but not for approximately 120 mv in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$. The limiting current density is somewhat higher for the reaction in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ than for the reaction in 85% H_3PO_4 - approximately $10 \mu\text{a}/\text{cm}^2$.

Electrochemical oxidation of propane at ambient temperature - current-potential diagram

Figure 5 shows the current density-potential plot for the oxidation of propane in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ at room temperature. These results can be compared in a general way to the oxidation of propane in 85% H_3PO_4 .

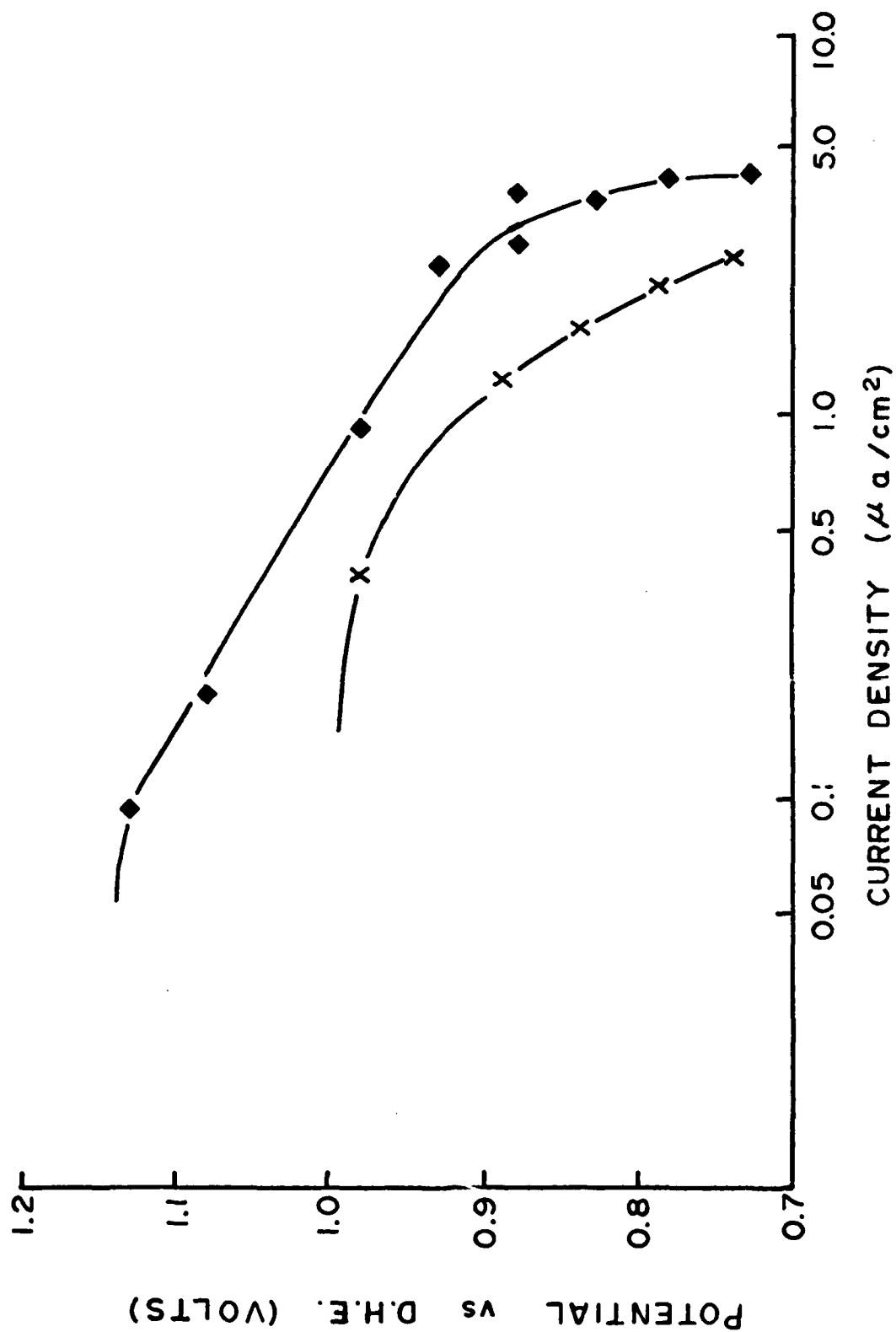


Figure 3. Current-potential diagrams for the air electrode at 25°C. X, 85% H_3PO_4 ; ◆, $CF_3SO_3H.H_2O$.

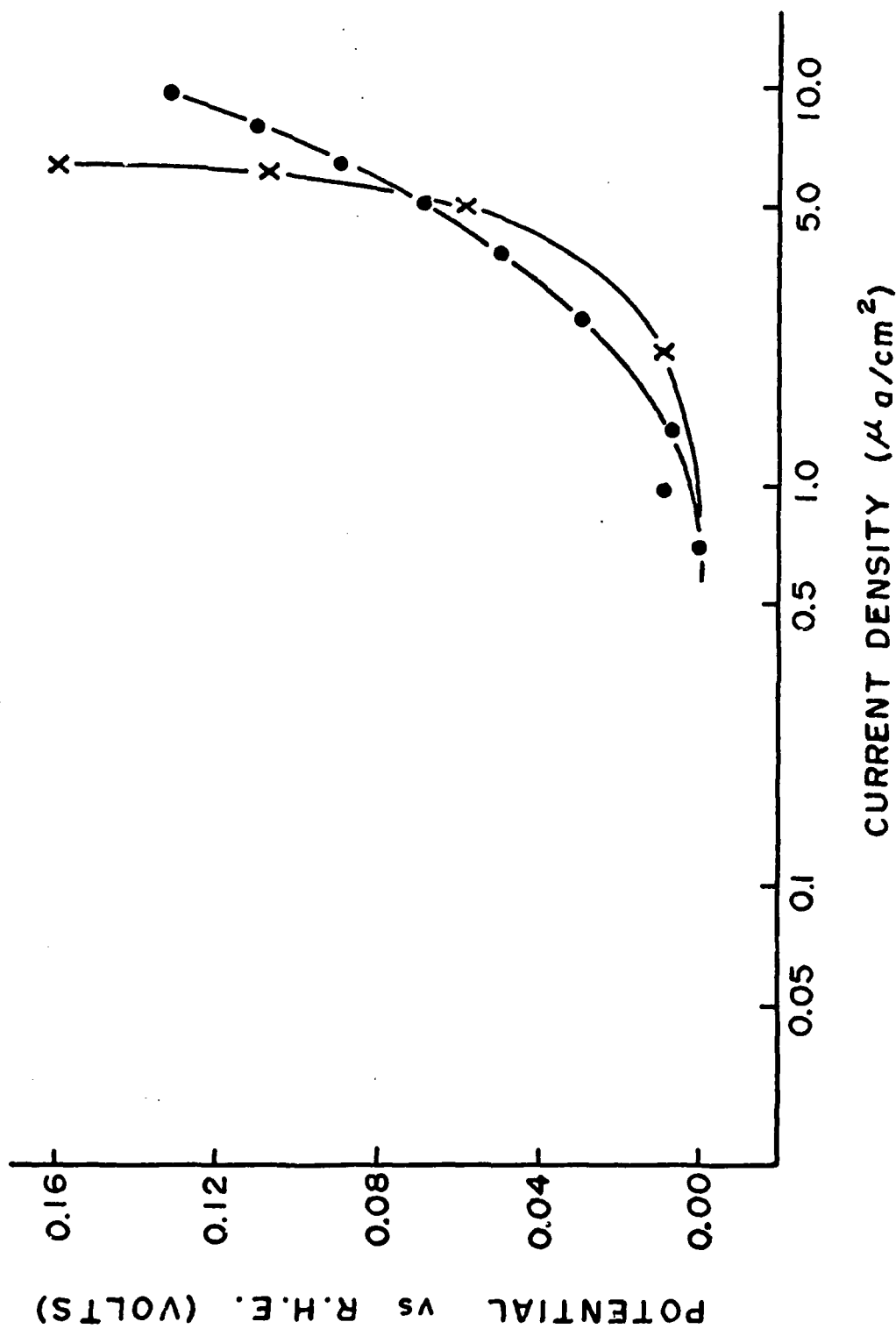


Figure 4. Current-potential diagrams for the hydrogen electrode at 23°C. X, 85% H_3PO_4 ; ●, $CF_3SO_3H.H_2O$

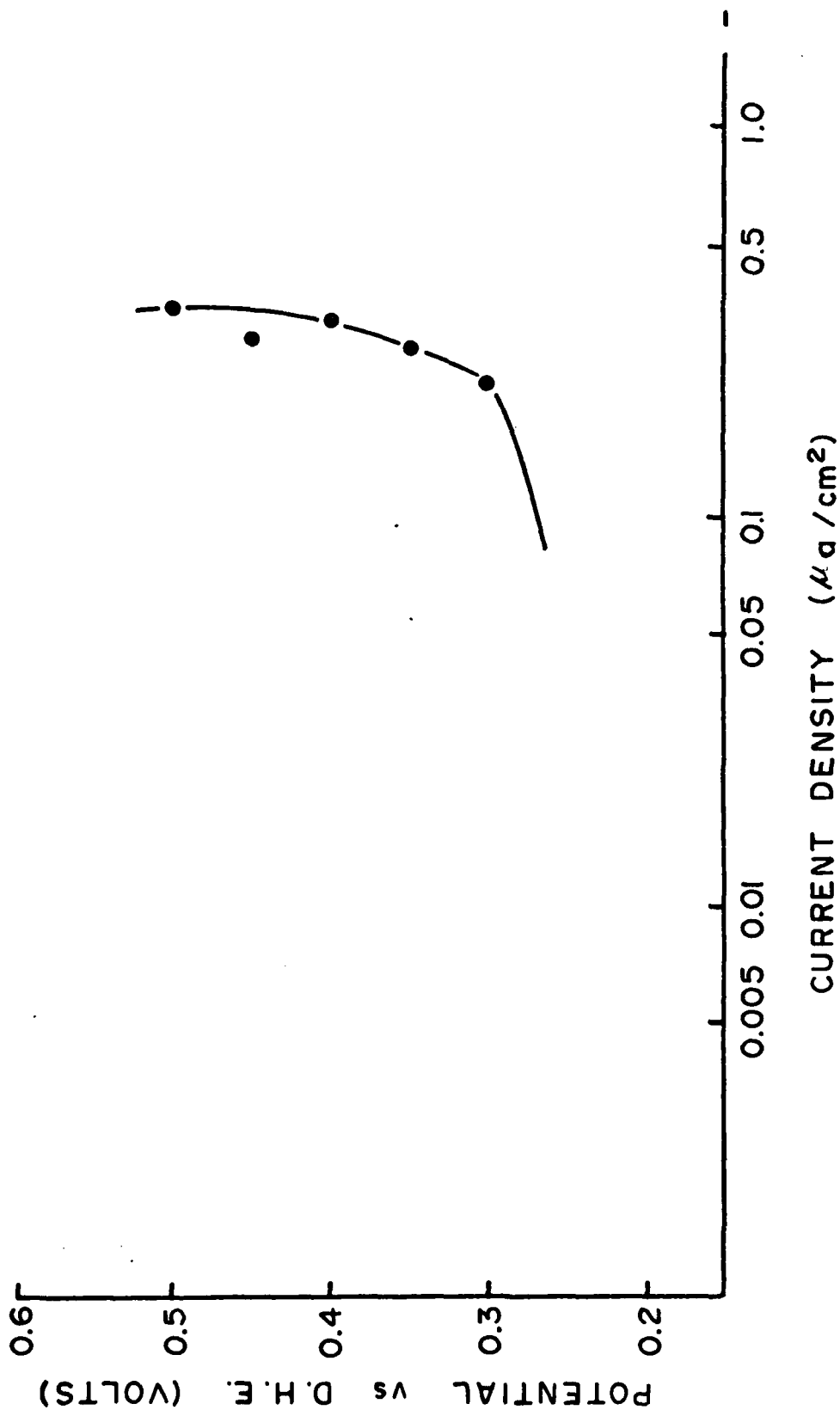


Figure 5. Current-potential diagrams for the electrooxidation of propane in $CF_3SO_3H \cdot H_2O$ at $23^\circ C$.

The conductivity of phosphoric acid at room temperature is quite low and the current values were low and erratic. The open circuit potential is approximately 0.28 volts and the limiting current density is approximately $0.37 \mu \text{ a/cm}^2$ for the oxidation of propane in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$.

Electrooxidation of methanol

The use of methanol as a fuel in a fuel cell system is attractive due to its low cost, ease of purification, and "clean" oxidation. Methanol was run as the fuel over a temperature range of 23° to 135°C . The air reaction was also run in the presence of methanol from 23° to 115°C .

Figure 6 shows the potential-current density plots for the electro-oxidation of methanol (concentration one molar) at 23° , 80° , 115° , and 135°C in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$. Also shown in this figure are the results reported by Bagotzky and Vassiliev (5) for one molar CH_3OH in $1\text{N H}_2\text{SO}_4$ at 80°C . At 23°C the open circuit potential is 0.4 volts and the limiting current density is $0.29 \mu \text{ a/cm}^2$. Obviously the electrochemical activity of the system is quite low at ambient temperatures. At 80°C the open circuit potential is 0.375 volts and the limiting current density is about $4.0 \mu \text{ a/cm}^2$. At 80°C the system was quite stable over a number of days indicating little loss of methanol due to vaporization from the cell containing a solution that was originally one molar in methanol. At 115°C the open circuit potential was 0.364 volts and the limiting current density about $2.2 \mu \text{ a/cm}^2$. Some deterioration of current at a set potential over time was observed. The loss of methanol due to vaporization was a possible explanation for these results. At 135°C the open circuit potential was 0.365 volts and the limiting current

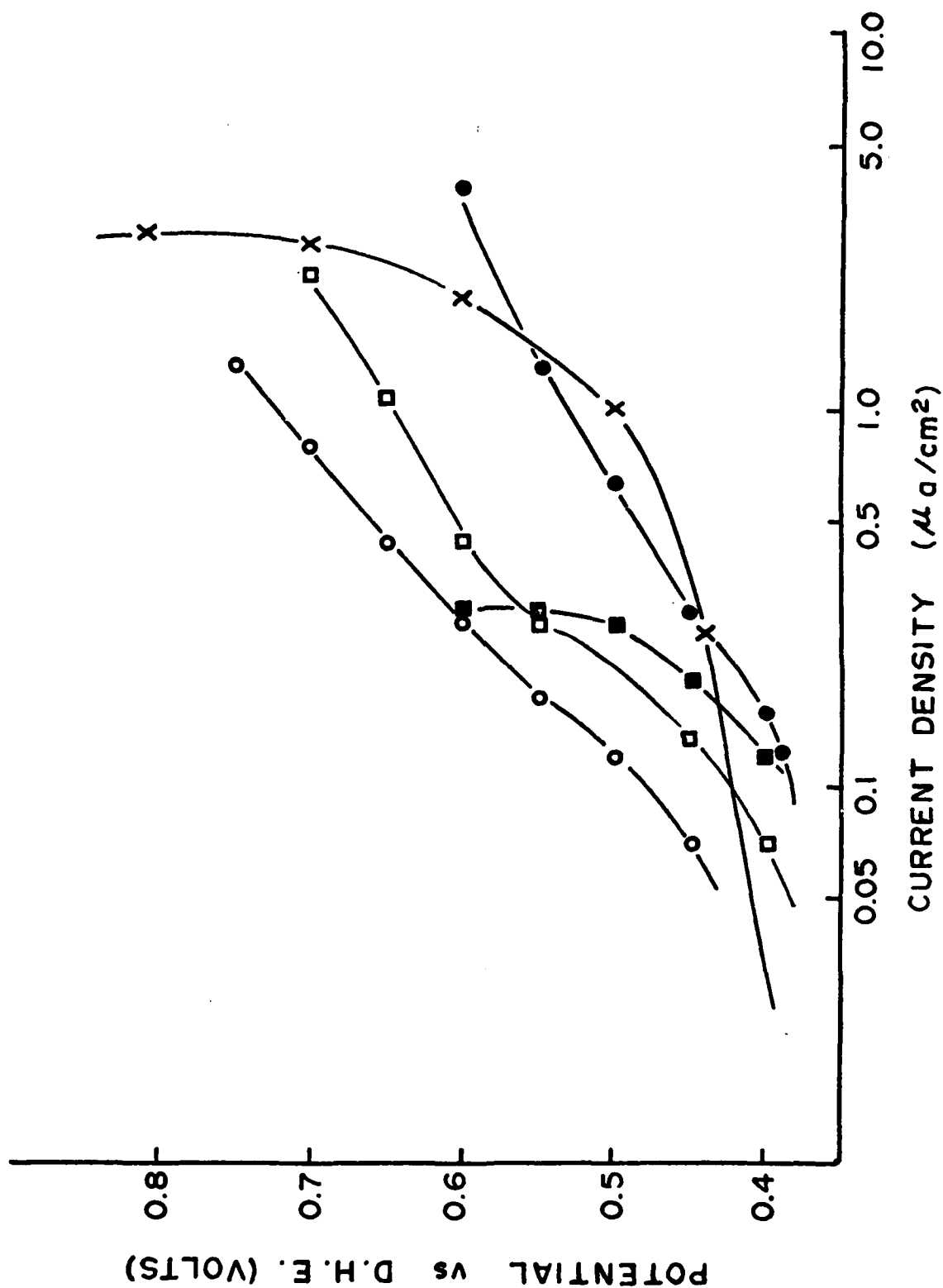


Figure 6. Current-potential diagrams for the electrooxidation of methanol. ■, 23°C; ●, 80°C; □, 115°C; ○, 135°C; x data from reference 5.

density was $1.33 \mu \text{ a/cm}^2$ for freshly prepared solutions. The current density values were not reproducible from run to run, decreasing with time. After two days no electrochemical activity was evidenced by the solution. A second methanol-electrolyte solution of the same methanol concentration was prepared and similar results were observed at 135°C . From these experiments it was concluded that the vaporization of methanol became excessive at temperatures above 100°C . The nmr examination of solutions from cells held at 115° to 135°C showed a decline in height of the CH_3 peak from that measured in the initial one molar solution. This was indicative of a lowering of concentration of available CH_3 group in the electrolyte.

From the results obtained to date it is concluded that the anodic reaction of methanol must be carried out at a temperature below 100°C . However the optimum temperature has not yet been determined. The results indicate the greatest electrochemical activity for methanol to be at 80°C .

The methanol-air fuel cell has been treated thermodynamically (6). Calculations based on heats of reaction indicate that a cell will be maintained at 60°C by the exothermic heat produced in the cell. Thus the collection of data under 60°C is not encouraged. On the other hand the excess vaporization of methanol above 100°C would argue against going to a higher temperature to get enhanced oxidation.

Methanol has been shown to interfere with the electroreduction of air or oxygen in H_2SO_4 (7). The air reduction in a 1M $\text{MeOH} - \text{CF}_3\text{SO}_3\text{H}$. H_2O solution was run at temperatures from 23 to 115°C .

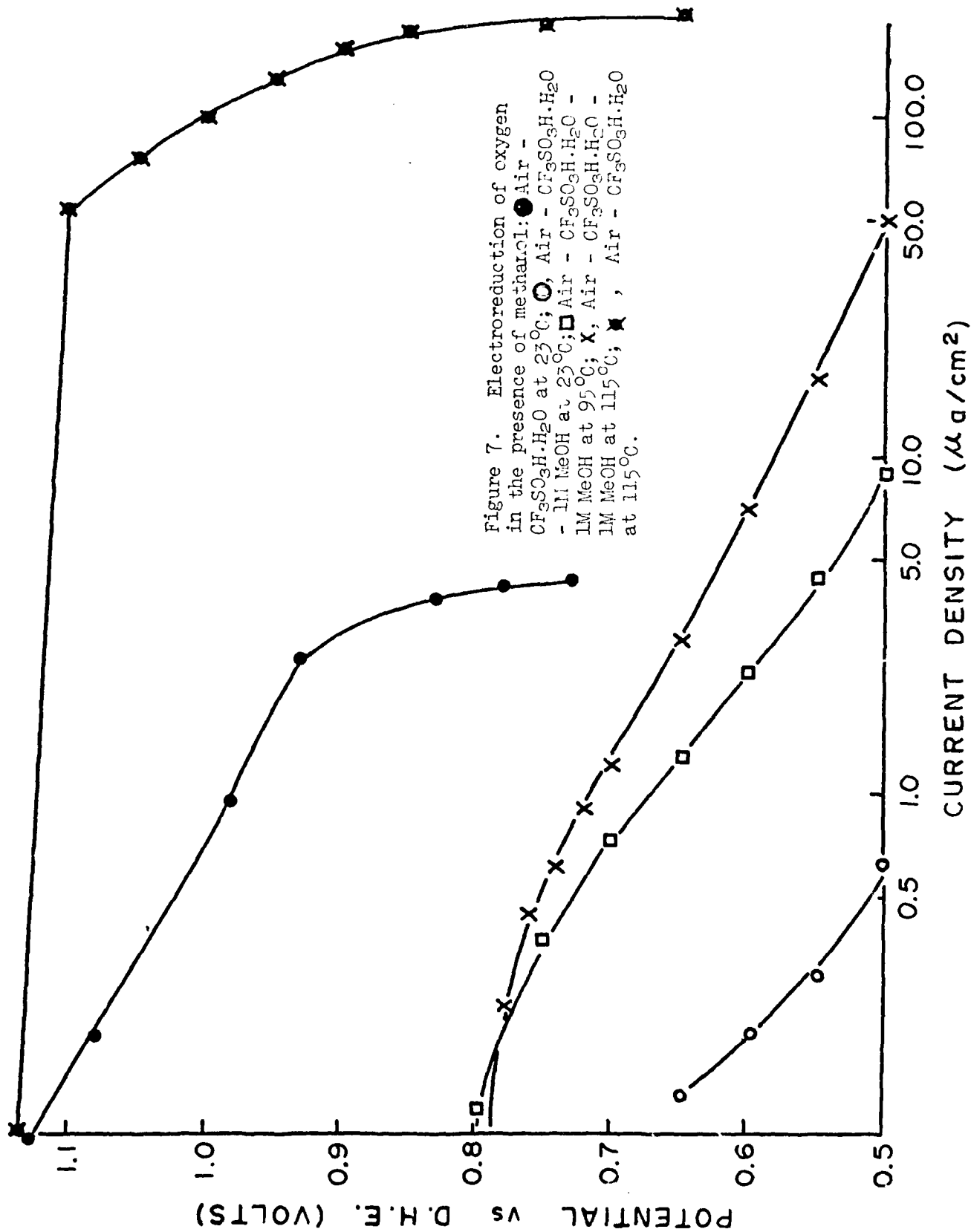
Figure 7 shows the electroreduction of air in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ and in 1M methanol- $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ at 23°C . Figure 7 also shows the electroreduction of air in 1M MeOH - $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ at 95° and at 115° compared to the electroreduction of air in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ in the absence of methanol at 115°C . The addition of 1M MeOH to $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ lowers the open circuit potential from 1.13 volts to approximately 0.78 volts. At any potential the current density for the air reduction is lowered by the addition of MeOH to the system. At 115°C there is less interference by the addition of 1M MeOH but it is still quite severe. These results correlate with those obtained in the experiments related to the anodic oxidation of MeOH. In those experiments, at higher temperatures, the rate of the electro-oxidation of methanol was reduced.

Both results can be explained on the basis of the undesirable, excessive, vaporization of methanol at elevated temperatures.

Nuclear Magnetic Resonance Measurements

The formation of esters by the reaction of $\text{CF}_3\text{SO}_3\text{H}$ and several alcohols has been reported in the literature (8,9). The reaction for $\text{CF}_3\text{SO}_3\text{H}$ and $\text{C}_2\text{H}_5\text{OH}$ is considered to be reversible at $\approx 150^\circ\text{C}$. (3) No information was found for the reaction of $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ and alcohols. Before electrochemical work was performed on the system, mixtures of methanol and $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ were examined at room temperature with nmr. The nmr results showed the acidic H peak and peak that would suggest the formation of the methyl ester (figure 8) as reported above.

Figure 9 shows a comparison of the nmr results for a known methyl peak from methyl alcohol and the unknown methyl peak from the methyl alcohol - $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ mixture. The peak for the methyl group from CH_3OH



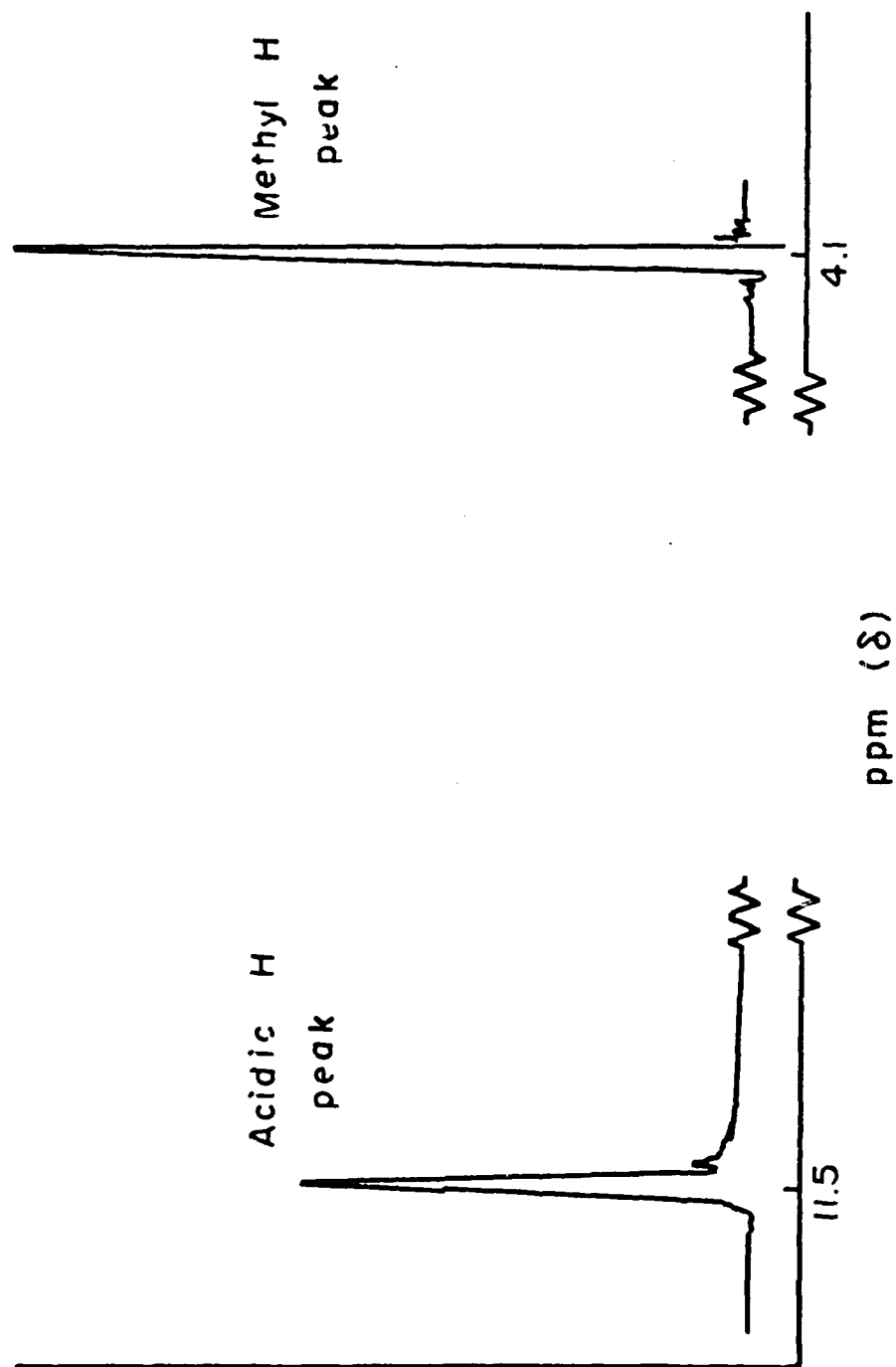


Figure 8. Pertinent parts of nmr spectra of solution of methanol in $\text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$.

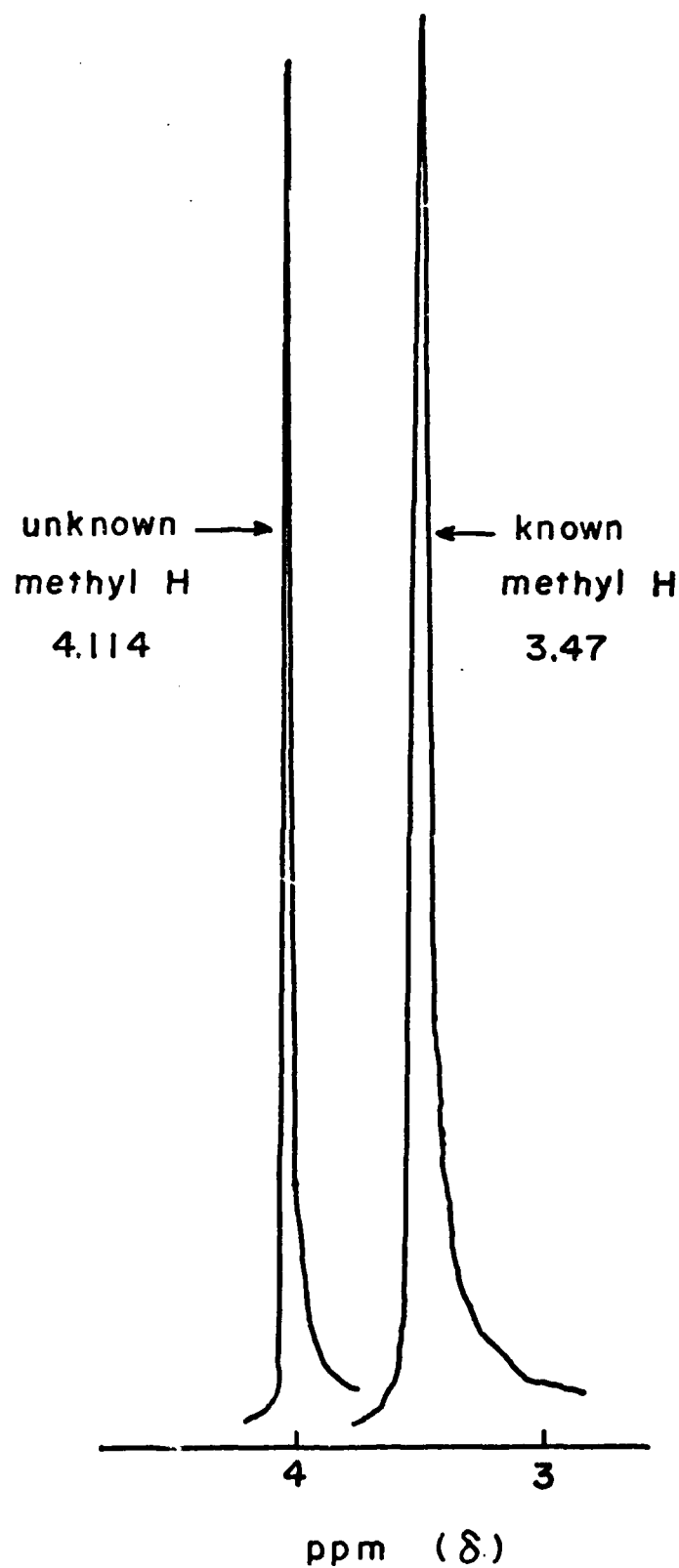


Figure 9. Comparison of peaks in nmr spectra. Right, methyl peak due to CH_3OH ; left, methyl peak due to one molar methanol- $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ mixture. Shift is 0.644 ppm.

occurs at 3.47 ppm. There is a shift of 0.644 ppm to 4.114 ppm for the CH_3 peak in the $\text{CH}_3\text{OH}-\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ mixture. This peak shift is convincing evidence for the formation of the methyl ester. There was no evidence of free methanol in methanol- $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ mixtures containing up to 20 molar methanol. The formation of the ester appeared to proceed completely at room temperatures and there was a rapid exchange of all methyl groups making them equivalent.

The correlation between peak height and the concentration of methanol added to the acid monohydrate could be established. From these data it is possible to determine the concentration of MeOH added to the system, or remaining after electrochemical oxidation in the half cell.

2.4 Conclusions

The feasibility of using methanol as a fuel has been examined. An nmr study indicates that methanol exists in the ester form in solution in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$. This esterification does not appear to inhibit the electrooxidation of methanol.* However, the excessive vapor pressure of methanol above 100°C does appear detrimental and it is suggested that future work be concentrated at a lower temperature such as 80°C . It has also been observed that methanol in the concentrations studied here lowers the open circuit potential of the air electrode. From these results additional experiments with methanol are warranted but it should be used as a gas with a diffusion electrode rather than as a dissolved liquid.

A series of experiments examined the electrochemical activity of hydrogen, propane, and air at ambient temperatures. In all cases limiting

* The possibility exists that the ester itself is electrooxidized but the work to date would not definitely indicate that it was or was not.

currents were significantly lower than those observed at higher temperatures but the current levels were such as to indicate that useful power might be produced at room temperature with these fuel cell reactions.

A further series of experiments studied the influence of the flow rate of air on the performance of the air electrode in $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$. It was established that electroactivity can be maintained at a relatively low flow rate and above a flow rate of 20 ml/min. the potential and limiting current are essentially insensitive to flow rate.

3.0 Future Work

In pursuit of the investigation of the two tasks set down in the Introduction it is intended to perform the following specific studies during the next reporting period.

a) The anodic reaction of methanol will be investigated at temperatures between 60 and 100°C to determine the optimum temperature for methanol oxidation.

b) The air reduction will be investigated with lower concentrations of methanol to determine what levels of methanol can be tolerated at the air electrode.

c) The investigation of the anodic oxidation of methane will be initiated.

d) A new cell design incorporating a diffusion electrode will be used to investigate the anodic oxidation of methanol from the vapor phase.

4.0 References

1. A.A. Adams, R.T. Foley and R.M. Goodman, Interim Technical Report No. 3 on Contract No. DAAK02-72-C-0084, June 1973.
2. A.A. Adams and R.T. Foley, Interim Technical Report No. 5 on Contract No. DAAK02-72-C-0084, July 1974.
3. T. Gramstad and R.N. Haszeldine, J. Chem. Soc., 1957, 4069.
4. A.A. Adams and R.T. Foley, Interim Technical Report No. 2 on Contract No. DAAK02-72-C-0084, February 1973.
5. V.S. Bagotzky and Yu. B. Vassilyev, Electrochimica Acta, 12, 1323 (1967).
6. C.E. Heath, Proceedings of the 17th Annual Power Sources Conference, pp. 96 (1963).
7. J.P. Hoare, J. Electrochem. Soc., 113, 846 (1966).
8. T. Gramstad and R.N. Haszeldine, J. Chem. Soc., 1956, 173.
9. A. Streitwieser, Jr., C.L. Wilkins, and E. Kiehlmann, J. Am. Chem. Soc., 90, 1598 (1968).